X-ray absorption near edge structure study using soft x-ray on ZnO/CdS interface for $Cu(In,Ga)Se_2$ thin film solar cell

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Photovoltaics is one of the promising renewable energy technologies to reduce global warming. There is, however, a crucial problem that the cost of the electrical energy generated by the solar cells was higher than that generated by fossil fuels. The cost reduction of solar cells is strongly required. For terrestrial applications, thin film solar cells are more advantageous than bulk type solar cells in terms of consumption of raw materials. In particular, $Cu(In,Ga)Se_2$ (CIGS) is an attractive material as an absorber layer for thin film solar cells because of a high optical absorption coefficient [1]. Research and development of CIGS thin film solar cells have been actively performed [2, 3].

Meanwhile, a CIGS thin film solar cell consists of heterostructures of various thin films. In thin film depositions of solar cell fabrication process, a sputtering method has been industrially used because of high throughput [4]. There is concern that the deposition of a window layer or a transparent conductive oxide layer by a sputtering method causes quality degradation of an underlayer because a kinetic energy of a deposited element is high. Although several groups suggested that a sputtering damage caused conversion efficiency degradation [4, 5], any physical changes of underlayers are not clarified. In this study, we focused on the i-ZnO/CdS interfaces which consist of i-ZnO layers deposited on a conventional CdS/CIGS/Mo/SLG (soda-lime glass) structure by the radio frequency (RF) magnetron sputtering method, and investigated a local structure at the i-ZnO/CdS interfaces.

A schematic illustration of the fabricated sample is shown in Fig. 1. An 800-nm-thick Mo layer was deposited on an SLG substrate by the RF magnetron sputtering method without intentional substrate heating. A 2.5-µm-thick CIGS layer was deposited by the three stage coevaporation method at the highest temperature of 550 ˚C [6]. In this study, the [Cu]/[Ga+In] and [Ga]/[Ga+In] composition ratios of the CIGS layer was estimated to be ~0.9 and ~0.3 from the results of energy dispersive x-ray spectrometry measurements, respectively. After CIGS surface cleaning by a KCN solution, the CIGS/Mo/SLG structures were annealed in N_2 ambient at 250 for 30 min. A 100-nm-thick CdS layer was deposited by the chemical bath deposition method. I-ZnO layers with various thicknesses were deposited by the RF magnetron sputtering method using a ZnO target (purity: 99.99 %). Prior to the deposition, the chamber was evacuated to a pressure of 2×10^{-4} Pa. A working pressure, a working gas, a sputtering power are 0.2 Pa, Ar, and 60 W, respectively. We controlled the i-ZnO thickness by varying the deposition time.

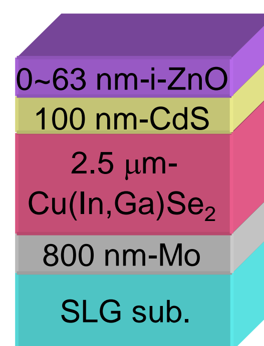

Fig. 1. Schematic illustration of fabricated samples.

We focused on X-ray absorption fine structure (XAFS) spectroscopy as an interface characterization method, because X-ray absorption near edge structure (XANES) spectroscopy is

a powerful technique for clarifying a local structure of a material. Soft X-ray XANES measurements were performed at BL-10 of the SR center at Ritsumeikan University, Japan [7]. S K-edge and Zn L_{III} and L_{II}-edge were measured at room temperature under vacuum conditions. In this experiment, double crystal monochromators of InSb(111) and Beryl($10\bar{1}0$) was utilized for S K-edge and Zn L_{II} & L_{III}-edge XANES measurements, respectively. We simultaneously performed partial fluorescence yield (PFY) and total electron yield (TEY) measurements for depth profiling.

S K-edge XANES spectra of the PFY measurements are shown in Fig. 2. Although i-ZnO thicknesses are varied, spectral changes are hardly observed in Fig. 2. S K-edge XANES spectra of the TEY measurements are shown in Fig. 3. The peak in the vicinity of 2473 eV becomes small as the i-ZnO layer thickness increases for the result of the TEY measurements. This result indicates that the surface parts of the CdS underlayer are amorphized [8]. In addition, the peak in the vicinity of 2482 eV becomes large as the i-ZnO layer become thick. We discuss this new peak. For comparison, the results of 500-nm-thick $ZnO_{1-x}S_x$ (zinc oxysulfide, x=0.18 and 0.53) layer, which is deposited on the CIGS/Mo/SLG structure by cosputtering of ZnO and ZnS targets [9], high purity $ZnSO_4•7H_2O$ and $CdSO_4•8H_2O$ reagents are shown. A remarkable peak appears at 2482 eV for $ZnSO_4•7H_2O$ and $CdSO_4•8H_2O$ which are sulfate compounds. On the other hand, a remarkable peak does not appear at 2482 eV for both the $ZnO_{1-x}S_x$ cases. We found that some sulfate compounds exists in the vicinity of the i-ZnO/CdS interfaces.

Zn L_{III} and L_{II}-edge XANES spectra of the TEY measurements are shown in Fig. 4. As the i-ZnO layer become thin, the pre-edge similar to the $ZnSO_4•7H_2O$ reagent in the vicinities of 1015 and 1037 eV becomes remarkable. Consequently, we found that $ZnSO_4$ formed in the vicinity of the i-ZnO/CdS interface rather than ZnS and $ZnO_{1-x}S_x$. Since the spectrum of the

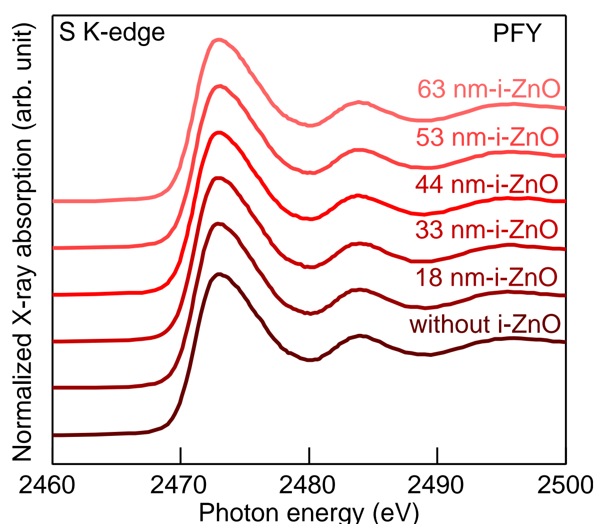

Fig. 2. S K-edge XANES spectra of PFY measurements.

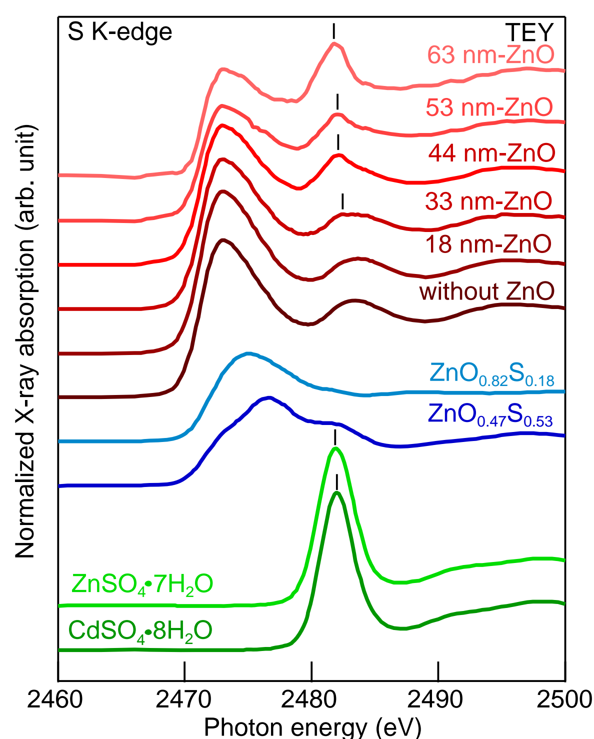

Fig. 3. S K-edge XANES spectra of TEY measurements.

5-nm-thick i-ZnO is quite similar to that of the 110-nm-thick i-ZnO, the composition change of the i-ZnO/CdS heterointerface is precipitous. On the other hand, we measured Cd L_{III} and L_2-edge XANES spectra though the spectra were not shown. In fact, remarkable spectral changes due to a sulfate and the amorphous components are not observed even in the TEY measurement results.

We investigated the local structure of the i-ZnO/CdS interface by the XANES measurements. We found that the surface parts of the CdS underlayer are amorphized. In addition, we found that at least $ZnSO_4$ formed in the vicinity of the i-ZnO/CdS interface. Moreover, the composition change of the i-ZnO/CdS interface is precipitous. XANES spectroscopy is therefore a powerful technique for investigating a local structure of the interface.

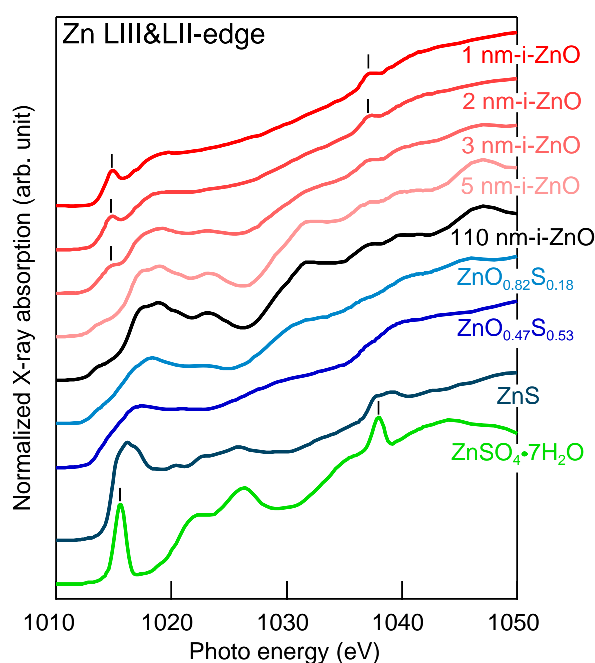

Fig. 4. Zn L_{III} and L_{II}-edge XANES spectra of TEY measurements.

Acknowledgements

The authors are grateful to Dr. T. Negami of Panasonic Electric Works Co., Ltd., for useful discussion. XAFS measurements of this work were supported by Nanotechnology Network Project of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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